



Lloret, E., Dessert, C., Buss, H. L., Chaduteau, C., Huon, S., Alberic, P., & Benedetti, M. F. (2016). Sources of dissolved organic carbon in small volcanic mountainous tropical rivers, examples from Guadeloupe (French West Indies). *Geoderma*, 282, 129-138.
<https://doi.org/10.1016/j.geoderma.2016.07.014>

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[10.1016/j.geoderma.2016.07.014](https://doi.org/10.1016/j.geoderma.2016.07.014)

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**Sources of dissolved organic carbon in small volcanic mountainous tropical rivers,
examples from Guadeloupe (French West Indies).**

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Abstract

In the tropical zone, small watersheds are affected by intense meteorological events. These events play an important role in the erosion of soils and therefore on the sources of organic carbon in small tropical rivers. We studied the geochemistry of two soils (ferralitic soil and Andosol) on Basse-Terre Island (French West Indies, FWI) by measuring dissolved organic carbon (DOC) of soil solutions, total organic carbon (TOC), total nitrogen (TN) concentrations in soil, carbon isotopic compositions of soil organic matter (SOM) and soil solutions, and organic matter characteristics of soil solutions (percent of organic carbon aromatic and hydrophobic). The two studied soils are very similar in terms of SOM and soil solution parameters. The TOC and TN contents vary between 1.7 and 92 g kg⁻¹ and, between 0.1 and 5.5 g kg⁻¹, respectively, with the highest concentrations observed in the topsoil. The C/N ratios are relatively constant throughout the soil profiles (ca. 12). The carbon isotopic composition of SOM varies between -27.3 and -22.7 ‰ and presents an enrichment with increasing depth of soil profiles. DOC concentrations in soil solutions, varying from 3.2 to 91.3 mg L⁻¹, are similar for the both extraction used in lab (with milliQ water and Ca(NO₃)₂) but are higher than those measured in soil solutions sampled from lysimeters (0.65-1.46 mg L⁻¹). The isotopic compositions of DOC obtained by extractions and SOM are comparable, with $\delta^{13}\text{C}$ values ranging from -28.6 to 25.8 ‰. The DOC sampled from lysimeters is systematically depleted in ¹³C compare to DOC obtained by extractions, with $\delta^{13}\text{C}$ values of -33.8 to -30.6 ‰. The enrichment of $\delta^{13}\text{C}$ of SOM along the soil profiles is either consistent with the carbon isotopic fractionation of SOM by decomposing organisms, or the differential mineralization of both labile and stable carbon stocks in soils, or the lixiviation of ¹²C-enriched soil layers. The $\delta^{13}\text{C}_{\text{DOC}}$ of water river samples and soil solutions obtained by extraction and collected with lysimeters demonstrates that the DOC in rivers derives

essentially from both the lixiviation of the soil surface layers during floods and groundwater flow during low water levels.

Keywords: Organic carbon sources, SOM, soil solution, DOC, small tropical rivers

1. Introduction

Rivers represent the major export of carbon from continents to oceans, with a global carbon flux (dissolved and particulate, organic and inorganic carbon) of 400-900 Mt yr⁻¹ (Hedges et al., 1997; Schlünz and Schneider, 2000; Aitkenhead-Peterson et al., 2003). The organic contribution (dissolved and particulate) represents about 40 % of the global continental carbon flux (Hedges et al., 1997; Schlünz and Schneider, 2000; Aitkenhead-Peterson et al., 2003). Locally, the contribution of organic carbon could be higher than that of inorganic carbon. This is notably observed for large tropical river systems (Huang et al., 2012), which have particular hydrological processes (Wohl et al., 2012), for which the dissolved form can represent more than 60 % of the total organic carbon export (Schlesinger and Melack, 1981; Hope et al., 1994; Ludwig et al., 1996a, 1996b). For small rivers directly connected to ocean basins with limited floodplains and mangroves, particulate organic carbon (POC) export is usually higher than dissolved organic carbon (DOC) export (Alvarez-Cobelas et al., 2012). Moreover, in mountainous tropical islands (e.g. Taiwan, New Zealand, Guadeloupe), the majority part of the organic carbon export occurs during flood events (Hilton et al., 2008a; Fujii et al., 2009; Bass et al., 2011; Lloret et al., 2013). Accordingly, the sources of organic carbon exported from the catchments vary with the hydrological stage, in particular for small rivers (Lloret et al., 2011).

Generally, the major sources of organic carbon in rivers are either autochthonous (DOC is directly produced in the river by biological activity) or allochthonous (detrital inputs) (e.g. Aitkenhead-Peterson et al., 2003; Mulholland, 2003; Finlay and Kendall, 2007). In the case of allochthonous sources, the main input is due to soil erosion. During erosive rainfall events, organic carbon contained in soil organic matter (SOM) can be intensively either leached or

eroded and transferred to aquatic ecosystems in dissolved and particulate forms, respectively (Lal, 2004). During low water stages, DOC input to rivers can also be completed by soil water infiltration. With 1400-1500 Gt of carbon, the SOM pool is one of the major carbon surface reservoirs (Schlesinger, 1977; Gregory et al., 1999) and stores twice the quantity of carbon contained in the vegetation. Accordingly, changes in SOM abundance and composition have important effects on the global carbon cycle as well as on soil ecosystems.

The organic matter amounts in soils are essentially regulated by the biological production and the decay rates of organic compounds. Plant residues (litter) falling onto soil surface are gradually decomposed through physical fragmentation, faunal and micro-faunal interactions (decomposers), mineralization and humus formation (Baudin et al., 2007). The overall processes induce variations in the concentration and in the isotopic composition of TOC along the soil profile. The decomposition of litter and SOM induces a differential decrease of carbon and nitrogen contents in soils. As they are not recycled at the same rate, the C/N ratio also varies along the soil profile. They are typically higher in litterfall and decrease in SOM during humification (Snowdon et al., 2005; Boström et al., 2007; Yang et al., 2010). Selective degradation changes the stable C isotope ratios of SOM. Surface litter remains more depleted in ^{13}C than SOM (Lichtfouse et al., 1995) that is progressively enriched in ^{13}C with soil depth (Balesdent and Mariotti, 1996; Amiotte-Suchet et al., 1999, 2007). Highlighting the variations in concentrations and isotopic compositions of TOC (in solid and solute fractions) in soils could help to track the origin of organic carbon in small tropical rivers with respect to their hydrological stages (low or high water stages).

In this way, Guadeloupean soils and rivers provide a remarkable opportunity to investigate the interactions between soil and river pools and fluxes (e.g. Rivé et al., 2013). The island of Guadeloupe, which presents surface soil horizons thoroughly enriched in organic matter (10-15 %; Colmet-Daage and Bernard, 1979), is frequently impacted by high intensity meteorological events such as tropical storms and cyclones (Zahibo et al., 2007) that accentuate the soil erosion (Waterloo et al., 2006; Dawson et al., 2008; Hilton et al., 2008b;

Lloret et al., 2011; Allemand et al., 2014). In order to determine the sources of DOC in Guadeloupean rivers, the present study focuses on the characterization (especially concentrations, and isotopic compositions) of organic carbon in SOM and soil solutions along soil profiles for different hydrological stages (flood or low water level) of two small watersheds with contrasted settings.

2. Study Areas

Guadeloupe is a part of the Lesser Antilles volcanic arc (Figure 1), generated by the subduction of the North American plate beneath the Caribbean plate. The volcanic island of Basse-Terre, part of the Guadeloupe archipelago, belongs to the central segment of the arc (e.g. Feuillet et al., 2011). Basse-Terre Island is characterized by old geological formations in its northern part and increasingly recent ones near the present-day volcano: La Soufrière, which is located in its southern part (Samper et al., 2007 and 2009). Our study is focused on two watersheds with different soil and river characteristics (Table 1), one located in the northern part of the island and another in the southern part (Figure 1). These two watersheds are located in the National Park of Guadeloupe, and are monitored within the framework of the French Critical Zone Observatory OBSERA (INSU-CNRS) observatory devoted to the study of weathering and erosion in the French West Indies. This observatory belongs to the French network of monitored watersheds (RBV supported by INSU-CNRS and AllEnvi).

2.1. Climate and hydrology

Basse-Terre Island is characterized by a wet tropical climate, with a mean annual temperature and humidity of ca. 23 °C and 75 %, respectively (Plaisir et al., 2003). The average annual precipitation of the last years ranges from 1500 to 7000 mm yr⁻¹, depending on the topography (Clergue et al., 2015; Dessert et al., 2015). Climate is characterized by two seasons: a dry season from January to June and a wet and rainy season from July to December. During the wet season, hurricanes and tropical depressions produce heavy rainfall events (Zahibo et al., 2007), which play a major role for soil weathering and erosion. The spatial distribution of precipitation is strongly influenced by easterly winds and topography.

The Bras-David and the Capesterre watersheds are located on the windward coast influenced by easterly winds and high annual precipitation, between 2000 and 4300 mm yr⁻¹ (Météo France data). Runoff represents about 60 % of the precipitation. The discharges of the studied rivers is monitored by DREAL (French Water Survey agency; <http://www.hydro.eaufrance.fr>).

2.2. Vegetation cover, geology and soils

Located in the National Park of Guadeloupe, the vegetation cover of the two studied watersheds is mainly tropical rainforest and is dominated by C3 photosynthetic pathway plants, including *Dichapetalaceae* (*Tapura latifolia*), *Euphorbiaceae* (*Richeria grandis*, *Amanoa caribaea*), *Burseraceae* (*Dacryodes excelsa*), *Sapotaceae* (*Pouteria pallida*) and *Annonaceae* (*Guatteria caribaea*) (Rousteau, 1994, 1996).

The geological basement of the Bras-David watershed is composed of Pleistocene andesitic and dacitic (Samper et al., 2007, 2009), and covered by thick ferralitic soils (> 15 m; Colmet-Daage and Bernard, 1979). These soils were previously studied (Henriet et al., 2008; Buss et al., 2010; Sak et al., 2010; Opfergelt et al., 2012; Clergue et al., 2015) and consist of highly weathered volcanoclastic debris flows containing rocky clasts at various stages of weathering. Clays, dominantly halloysite, represent about 75 % wt of the mineralogical content and nonclays are almost entirely Fe(III)-hydroxides and quartz/cristobalite. The Capesterre watershed is underlain by andesitic rocks linked to late Pleistocene volcanism (Samper et al., 2007). Because of the steep slopes of the recent volcanic rocks (49 %; Plaisir et al., 2003), soils in this region are dominated by thin Andosols (< 1 m; Colmet-Daage and Bernard, 1979; Cattani et al., 2007; Cabidoche et al., 2009).

3. Materials and methods

3.1 Sample collection

3.1.1 Litter and soil material sampling

Two soil cores, representative of the two main soil types (ferralitic and Andosol) were sampled to analyze the total organic carbon (TOC) and total nitrogen (TN) concentrations and

the stable carbon isotope composition ($\delta^{13}\text{C}$) of litter and SOM. The soil profiles were sampled every ~15 or ~30 cm (1/2 foot or 1 foot), with a hand-auger at 0.15-0.91 m and 0.15-12.50 m soil depths for Capesterre and Bras-David watersheds, respectively. In addition, larger amounts of topsoil layers (from 0 to 30 cm) were also sampled every 5-10 cm in pits. All soil samples were air-dried, sieved to 2 mm, split with a sample divider and homogenized by grinding at the USGS Menlo Park Campus (California, USA). Litter material from the two watersheds was collected in plastic bags and was rapidly air-dried to avoid mould development, then ground.

3.1.2 Soil solution sampling

Vadose zone pore waters were collected approximately monthly during 2007 and 2008 from 5 cm diameter nested porous-cup suction water samplers (Soil Moisture Inc., Santa Barbara, CA) (referred to as lysimeters hereafter). These lysimeters were placed in hand-augered holes at depths from 0.15 to 0.91 m and from 0.15 to 12.50 m for Capesterre and Bras David sites, respectively. Soil solution characteristics were obtained by extracting soils with milliQ water following the procedure in Bardy (2008) or using a $\text{Ca}(\text{NO}_3)_2$ solution at 4.6×10^{-3} M according to Zsolnay (2003). The solution/soil ratio and the time of extraction are reported in Table 2. Soil solution samples used for DOC concentrations and $\delta^{13}\text{C}$ measurements were filtered through glass fiber filters (GF/F Whatman® by Schleicher & Schuell cut off 0.7 μm) and acidified with concentrated H_3PO_4 (85 %) in pre-cleaned and pre-combusted glass bottles, and stored at 4 °C in the dark.

3.1.3 River sampling

Pristine water samples were collected upstream of any anthropogenic activities. Surface water was sampled manually from 2007 to 2010 at different hydrological stages corresponding to low water and flood levels (Lloret et al., 2011, 2013; Dessert et al., 2015). An automatic water sampler, ISCO-6712, was set up on the Capesterre River to sample the largest number of extreme meteorological and hydrological events. It allowed the sampling of 27 flood events

including 5 extreme events during which up to 24 samples were taken (from every 15 min to 2 h). Water samples used for the measurement of DOC concentrations and $\delta^{13}\text{C}$ measurements were filtered, acidified and stored as for soil solution sampling.

3.2 Analytical methods

TOC and TN concentrations of litter and SOM were measured using an elemental analyzer (Thermo Scientific Flash 2000), after checking that samples are carbonates free (controlled under acid vapor). The detection limit was $< 5 \%$.

The $\delta^{13}\text{C}_{\text{TOC}}$ were measured twice:

- at the Laboratoire de Géochimie des Isotopes Stables (LGIS, IGP, France), using an IR-MS Finnigan MAT 253 coupled with an elemental analyzer *Thermo Flash EA 1112 Series*.
- at the Institut d'Ecologie et des Sciences de l'Environnement de Paris (iEES, UPMC, France), using an IR-MS Sira 10 Fisons coupled with an elemental analyzer Carlo-Erba Na-1500 NC.

Results are reported in per mil (‰) relative to the Pee Dee Belemnite (PDB) standard with an analytical precision of 0.3 ‰. Because results of the two labs are very similar, data reported in this study are averages of these two measurements.

The DOC concentrations from soil solutions or river waters were measured using a Shimadzu TOC-VCSH analyzer (Sugimura and Suzuki, 1988). The detection limit was 0.24 mg l^{-1} and the precision was 2 %. The $\delta^{13}\text{C}_{\text{DOC}}$ was measured at the “Institut des Sciences de la Terre d'Orléans” (ISTO, France) with an IR-MS Delta V Advantage coupled with a LC-Isolink interface (both Thermo Scientific) and a HPLC system serving as a pump for the carrier flow. Aliquots of $100 \mu\text{L}$ of filtered and acidified sample water were directly injected in bulk mode and monitored in continuous flow (Albéric et al., 2010). The standards used for the $\delta^{13}\text{C}_{\text{DOC}}$ measurements were the internal standard from ISTO (NaHCO_3 , -4.3 ‰), a benzoic acid (-25.7 ‰), USGS-40 (L-glutamic acid, -26.389 ‰), IAEA-C8 (oxalic acid, -18.3

‰) and IAEA-C6 (sucrose, -10.8 ‰). The precision of DOC isotopic compositions was 0.3 ‰.

Spectrophotometric analyses of liquid samples were conducted with a dual beam Evolution 600 UV/Vis – Thermo Scientific spectrophotometer. An aliquot of each acidified water sample collected for the DOC measurements was used for the spectroscopic characterization of the dissolved organic matter (DOM). Samples were placed in a 1 cm quartz window “cuvette” and scanned from 200 to 600 nm, with 1 nm resolution (Chin et al., 1994). The percentages of aromatic carbon and the hydrophobic fraction of DOM were estimated from the UV-Vis absorbance data, with empirical relationships (Chin et al., 1994). Different wavelengths were selected (254, 270, and 280 nm) to highlight the markers of organic matter. The absorbance at these different wavelengths defined as SUVA (Specific UV absorbance) is calculated with the following formula:

$$\text{SUVA}_i = \frac{\text{Absorbance at wavelength } i \text{ (cm}^{-1}\text{)}}{\text{DOC concentration (mg L}^{-1}\text{)}} \quad (\text{i.e. SUVA}_{254}, \text{SUVA}_{270}, \text{SUVA}_{280}) \quad (1)$$

4. Results

4.1 Organic carbon and total nitrogen distributions along soil profiles

4.1.1 TOC and TN in litter and SOM

For the Bras-David site, the mean organic carbon and nitrogen contents in the litter layers are $395 \pm 3 \text{ g kg}^{-1}$ and $12.8 \pm 0.2 \text{ g kg}^{-1}$, respectively, corresponding to a C/N (or TOC/TN) ratio of 30.8 ± 0.6 (Table 3). For Capesterre, they averaged $409 \pm 6 \text{ g kg}^{-1}$ and $15.9 \pm 0.1 \text{ g kg}^{-1}$, respectively, corresponding to a C/N ratio of 25.8 ± 0.5 (Table 4). The TOC content of the Bras-David ferrallitic soil decreases within the top two meters ranging 92 to 1.7 g kg^{-1} (Table 3). For soil depths between 2.0 and 12.5 m, the TOC content is $< 3.7 \text{ g kg}^{-1}$ (range: ca. 0.9-3.7). Similarly, TN contents are higher within the top two meters (range: ca. 0.1-5.5 g kg^{-1}), a decrease to 0.1 g kg^{-1} for deeper horizons. Consequently the C/N ratio remains relatively constant along the soil profile (ca. 12.7 ± 3.2) (Table 3). For the Capesterre soil, the highest TOC and TN contents are found in the topsoil (0.00-0.20 m depth) where they reached more

than 23.6 g kg⁻¹ and 2.3 g kg⁻¹, respectively, then they decrease progressively to 5.6 g kg⁻¹ and 0.4 g kg⁻¹, respectively, in 0.20-0.91 m soil horizons (Table 4). As in the Bras-David ferrallitic soil, the C/N ratio in the Capesterre Andosol remains constant along the soil profile (ca. 11.4 ±1.4) (Table 4).

The TOC and TN stocks for the upper 30 centimeters were calculated from concentrations (C), dry densities ($d = 0,650$ and $0.875 \cdot 10^3 \text{ kg m}^{-3}$ for 0-15 cm and 15-30 cm, respectively; Buss et al., 2010) and thicknesses (t) of each horizon, using the following formula:

$$\text{Stock} = C \cdot d \cdot t \quad (2)$$

TOC and TN stocks in the Bras-David ferrallitic soil are almost 11,600 and 800 Mg km⁻², respectively, and in the Capesterre Andosol are almost 11,200 and 1000 Mg km⁻², respectively.

The carbon isotopic composition of SOM for the Bras-David ferrallitic soil and the Capesterre Andosol varies between -27.3 and -24.2 ‰ (Tables 3 and 4) and is representative of degraded and humified ¹³C-enriched organic matter derived from trees and understory C3 photosynthetic pathway plants (Deines, 1980; Balesdent et al., 1993) that compose the Guadeloupean rainforest. Additional evidence is pictured by the even more ¹³C-depleted (less degraded) composition of litterfall for both soils (ca. -29.0 - -29.7 ‰, Tables 3 and 4).

4.1.2 DOC in soil solutions

The DOC concentrations in soil solutions obtained by milliQ water and Ca(NO₃)₂ extractions are similar and follow the same trends along the two soil profiles (Tables 3 and 4). For the Bras-David ferrallitic soil, the DOC concentrations decrease with depth from 91.3 to 5.2 mg l⁻¹ within the upper two meters, and remain constant below 2 m with a value of $5.8 \pm 1.5 \text{ mg l}^{-1}$ (Table 3). For the Capesterre Andosol, the DOC concentrations range from 3.2 to 28.9 mg l⁻¹ (Table 4), exhibiting the highest values within the upper 30 centimeters and decreasing with depth.

The DOC concentrations in soil solutions sampled from lysimeters are lower than those obtained by soil extractions, but the trends along the two soil profiles are similar for both techniques (Tables 3 and 4). For the Bras-David ferrallitic soil, the DOC concentrations in soil solutions sampled by lysimeters decrease with depth from 1.46 to 0.65 mg l⁻¹ within the upper two meters, and remain constant (ca. 0.69 ± 0.08 mg l⁻¹) below 2 m (Table 3). For the Capesterre Andosol, the DOC concentrations in soil solutions decrease with depth from 1.45 to 0.88 mg l⁻¹ (Table 4).

For the two soil profiles, the isotopic compositions of DOC obtained by extractions and SOM are comparable, with $\delta^{13}\text{C}$ values ranging from -28.6 to -26.3 ‰ and from -28.3 to -25.8 ‰ for the soil solutions of Bras-David ferrallitic soil and the Capesterre Andosol, respectively (Tables 3 and 4). The DOC sampled from lysimeters is, however, systematically depleted in ¹³C compare to DOC obtained by extractions, with $\delta^{13}\text{C}$ values of -33.8 to -31.2 ‰ and -33.1 to -30.6 ‰ for the Bras-David ferrallitic soil and the Capesterre Andosol, respectively (Tables 3 and 4).

The percentage of aromatic organic carbon, or “aromaticity” of the dissolved organic matter (DOM) was calculated by averaging the values following the relationships for various DOM types from Chin et al. (1994), Peuravuori and Pihlaja (1997), and Weishaar et al. (2003). The DOM is more aromatic in soil solution sampled from lysimeters than those obtained by milliQ water extractions. In the lysimeter samples, the aromaticity is 18 to 33 % and 16 to 33 % for the Bras-David ferrallitic soil and the Capesterre Andosol, respectively. In milliQ water extractions, the aromaticity is 8 to 20.2 % and 7 to 14 %, for the Bras-David ferrallitic soil and the Capesterre Andosol, respectively (Tables 3 and 4). Similarly, we have also observed that the percentage of hydrophobic organic carbon (calculated following methods from Chin et al. (1994), and Weishaar et al. (2003)) for the two soil profiles is more significant for solutions collected from lysimeters than from extractions.

4.2 DOC in river waters

The DOC concentrations for the two studied Guadeloupean rivers were reported in studies of Lloret et al. (2011, 2013). These rivers exhibit comparable DOC concentrations, between 0.46 and 5.75 mg l⁻¹. During low water level the mean DOC concentrations are 0.76 ±0.28 mg l⁻¹ and 1.40 ±0.60 mg l⁻¹ for the Bras-David River and the Capesterre River, respectively. During flood events, the mean DOC concentrations are similar for both rivers, with 2.71 ±1.37 mg l⁻¹ for the Bras-David River and 2.24 ±0.66 mg l⁻¹ for the Capesterre River.

The isotopic compositions of DOC in the rivers range from -35.0 to -22.9 ‰, with δ¹³C values, which are more depleted in ¹³C during low water level than flood events.

For both rivers, the aromaticity ranges from 27 to 72 %, but no differences were observed between low water level and floods. Again, the percentage of hydrophobic organic carbon for both rivers is not related to hydrological levels, and ranges from 50.6 to 139.0 %.

5. Discussion

The following discussion will first focus on the characteristics of the Guadeloupean SOM, and then on the comparison between soil solutions sampled by lysimeters and obtained by extractions. Finally we will address the question of the sources of dissolved organic carbon according to the hydrological stages.

5.1 Production and evolution of SOM in volcanic tropical soils

For both sites, litter exhibits rather similar TOC (ca. 400 g kg⁻¹) and TN (ca. 14.5 g kg⁻¹) contents (Tables 3 and 4), which are close to those measured in other tropical forests (Schwartz, 1993). The C/N ratios for litter samples (25.8-30.8, Tables 3 and 4) are lower than those usually observed for litterfall in tropical forests (38-43; Schwartz, 1993), indicating that fresh organic matter had likely partly decayed in litterfall before incorporation into soil organic matter.

The TOC and TN contents and the C/N ratios are also similar for both soils (Tables 3 and 4), and are comparable to values measured in pristine forest soils in the East Kalimantan Province, Indonesia (Fujii et al., 2009), humid tropical primary forest soils in Sumatra (van

Noordwijk et al., 1997), and ferralitic soils under tropical rainforest originate from different countries around the world like Brazil, Indonesia, Zaire, ... (Kauffman et al., 1998). Several inferences can be made from these results:

- The decreases of TOC and TN contents and C/N ratios between litter and soils and with soil depth (Tables 3 and 4) reflect the ongoing decomposition-humification processes of organic matter in the soils.
- The low C/N ratios of the two Guadeloupean soils indicate a high degree of decomposition (Kauffman et al., 1998).
- The relatively constant C/N ratios along the two soil profiles indicate that organic carbon and nitrogen are degraded at a similar rate.

For the upper 30 centimeters of soil profile, the carbon stocks in the Guadeloupean ferralitic soil and Andosol (11,600 ad 11,200 Mg km⁻², respectively) are twice higher than values found for primary wet tropical forests (e.g. Baudin et al., 2007; Ngo et al., 2013). However, they are comparable to estimates given for soils of Martinique (13,000 Mg km⁻²; Blanchart and Bernoux, 2005). Moreover, Martinique and Guadeloupe islands are covered by the pretty similar tropical rainforest. These high carbon contents are probably due to soils are formed with similar volcanic rocks coming from the same volcanic arc.

Litters are more depleted in ¹³C than the upper 15 centimeters of both soils (Tables 3 and 4), a relationship which is generally observed worldwide (e.g. Ladyman and Harkness, 1980; Bellanger et al., 2004). During the decay of fresh organic matter (litter), the decomposers preferentially use the ¹²C, which results in ¹³C enrichment of the remaining SOM. Accordingly, SOM is typically ¹³C-enriched by 1.5-4.3 ‰ relative to homogenous plant and litter constituents (Lichtfouse et al., 1995).

For both soil profiles, the $\delta^{13}\text{C}$ values of SOM ($\delta^{13}\text{C}_{\text{SOM}}$) increased slightly (1.5 ‰) with depth within the top meter. This ¹³C enrichment is negatively correlated with the TOC content. These results are similar to those observed by Balesdent et al. (1993), Balesdent and

Mariotti (1996), for mainland French soils, and for other soils in equilibrium with C3 plants under tropical forests in Amazon basin (Andreux et al., 1990; Desjardins, 1991; Desjardins et al., 1994; Koutika et al., 1997). The observed pattern of ^{13}C enrichment over the top meter is typically interpreted as the stable carbon isotopic fractionation of SOM by decomposing organisms (Mariotti and Balesdent, 1990; Mariotti, 1991; Boutton, 1996), and is supported by the correlation between $\delta^{13}\text{C}_{\text{SOM}}$ and LnC for both soil profiles (Figure 2a). This enrichment is controlled by different factors such as the molecular characteristics of the initial material (Agren et al., 1996), the degree of SOM decay (Blair et al., 1985) and the diversity of decomposers (Andrews et al., 2000). Alternatively, a differential mineralization of two carbon stocks in the soils, one labile and one more stable (Mariotti, 1991), may be involved, as highlighted by the correlation between $\delta^{13}\text{C}_{\text{SOM}}$ and $1/\text{C}$ for both sites (Figure 2b). Finally, this trend may also result from the leaching of SOM by groundwater flow, which tends to preferentially remove the ^{12}C and leave a ^{13}C -enriched SOM residue (Kaiser et al., 2001). The extent of carbon isotopic variations of these two Guadeloupean soils may reflect: (1) the high clay content typical of tropical soils (Schulte and Ruhayat, 1998; Buss et al., 2010), (2) high net primary productivity, and so high soil microbial activity (Baudin et al., 2007) and, (3) high annual precipitation resulting in high percolation fluxes and high adsorption potential (Shen, 1999; Neff and Asner, 2001). For the Capesterre Andosol, the dominant process that can be put forward is likely carbon isotopic fractionation during SOM decay (better correlation coefficient than for mineralization, Figure 2). But for the Bras-David ferrallitic soil, it is hard to solve what is the dominant process, because the correlation coefficients (Figure 2) are quite similar for the two processes of carbon isotopic fractionation origin (SOM decay or mineralization).

5.2 DOC production and cycling in tropical volcanic soils

The DOC concentrations obtained by milliQ water and $\text{Ca}(\text{NO}_3)_2$ extractions are very similar and follow the same decreasing trend as the TOC (Tables 3 and 4). These similarities could be

explained by the extraction technique, which allow extracting the same fraction of dissolved organic matter. For the upper 30 centimeters, the Capesterre Andosol contains less DOC than the Bras-David ferrallitic soil, probably due to the enrichment of organic carbon in the surface layers of the Bras-David ferrallitic soil relative to the Capesterre Andosol. Moreover, ferrallitic soils are generally more acidic than Andosols (Colmet-Daage and Lagache, 1965), and thereby more effective at dissolving organic carbon. The dissolved organic matter in soil solutions collected by lysimeters could reflect the mobile fraction of organic matter (Zsolnay, 2003), whereas the extractions would extract both the mobile and immobile fractions (Zsolnay, 2003), explaining the higher DOC concentrations for the extractions (Tables 3 and 4).

The extracted soil solutions are generally more depleted in ^{13}C than SOM, except in the upper 30 centimeters (Tables 3 and 4). This likely reflects the preferential adsorption of carboxylic groups which are enriched in ^{13}C , leaving the soil solution depleted in ^{13}C (Kaiser et al., 2001; Garten et al., 2000). There is, however, a carbon isotopic difference in the DOC between the two types of extraction. For both soils, the extracted milliQ water solutions are generally more depleted in ^{13}C than the extracted $\text{Ca}(\text{NO}_3)_2$ solutions (Tables 3 and 4). This observation shows that different fractions of dissolved organic matter are extracted by these two methods. Conversely, for both sites, increasing $\delta^{13}\text{C}$ of SOM is observed with decreasing $\delta^{13}\text{C}$ of DOC in lysimeter solutions (Tables 3 and 4). This trend was also observed by Ludwig et al. (2000) and attributed either to the preferential decay of labile substances or to the selective adsorption of carbon. During SOM decay, the decomposers preferentially use ^{12}C , enriching the remaining SOM in ^{13}C (e.g. Andreux et al., 1990; Desjardins et al., 1994; Koutika et al., 1997; Amiotte-Suchet et al., 1999, 2007), and consequently depleting the soil solution produced in ^{13}C relative to SOM (Agren et al., 1996; Amiotte-Suchet et al., 2007). According to the second process the preferential adsorption of the carboxylic groups enriched

in ^{13}C (Kaiser et al. 2001) would also leave a soil solution depleted in ^{13}C (Garten et al., 2000).

The proportion of aromatic DOC is higher in soil solutions collected by lysimeters than in those extracted with milliQ water (Tables 3 and 4). In fact, dissolved organic matter in soil solutions obtained by milliQ water extraction can be represented by fulvic acids that are enriched in ^{13}C and less aromatic. The dissolved organic matter in soil solutions collected by lysimeters can be represented by humic acids (depleted in ^{13}C and more aromatic) (Nissenbaum and Kaplan, 1972; Flexor and Volkoff, 1977).

5.3 DOC sources in small tropical volcanic rivers

The DOC in stream waters results from the mixing of two sources, which are represented by soil solutions collected from lysimeters and by extractions (Figure 3). During flood stage (Lloret et al. 2011, 2013), the streams are essentially fed by lixiviation of soil surface layers (represented by extracted soil solutions). During low water levels (Lloret et al., 2011, 2013), the streams are fed by groundwater (represented by soil solution collected from lysimeters).

The two river samples, collected during low water levels, which have very low $\delta^{13}\text{C}$ and low 1:DOC ratio (Figure 3), can be attributed to additional sources, likely primary production in the rivers ($\delta^{13}\text{C}$ of phytoplankton in natural river waters is -35 to -25 ‰, Kendall et al., 2001) and the mineralization of leaves falling directly into the rivers ($\delta^{13}\text{C}$ of leaves is lower than of litter or soil, thus < -25.8 ‰), respectively. This interpretation is supported by the observation of a biofilm on river stones during the low water periods.

Conclusion

This study shows clearly that there are different sources of DOC according to hydrological stages of the Guadeloupean rivers. These sources are deeply related to processes occur in soils. TOC and TN decrease with depth in the bulk soil, whereas the C/N ratio remains relatively constant along the soil profile. The enrichment of $\delta^{13}\text{C}$ of SOM with depth along the soil profile is consistent with the carbon isotopic fractionation of SOM by decomposing

organisms, or the differential mineralization of both labile and stable carbon stocks in soils, or the leaching of SOM by groundwater flow.

The $\delta^{13}\text{C}_{\text{DOC}}$ of river water samples and soil solutions obtained by extraction and collected from lysimeters demonstrates that the DOC in rivers derives essentially from both the lixiviation of the soil surface layers during floods and from groundwater during low water levels. The dissolved organic matter in extracted soil solutions, which is represented by fulvic acids, is more enriched in ^{13}C and less aromatic than that from lysimeters, which is represented by humic acids. Another source with very low $\delta^{13}\text{C}_{\text{DOC}}$ and high 1/DOC ratios may also feed the rivers during low water levels. This additional source is likely to be either the internal primary production of the rivers or the mineralization of leaves that fall into the rivers. Further study of the $\delta^{13}\text{C}$ of biofilms formed on river stones during low water periods may help to better constrain this other source.

Therefore, three main sources of DOC in rivers were identified in the particular case of small tropical mountainous watersheds. As it was demonstrated by Lloret et al. (2013), the DOC yields of Guadeloupean rivers are close to those of large tropical rivers, like the Amazon or the Orinoco. Consequently, identification of several DOC sources is a crucial point to better understand global carbon cycle.

Acknowledgements

This work would not have been possible without the logistical support by two INSU-CNRS observatories run by IPGP: the Observatoire Volcanologique et Sismologique de Guadeloupe and the Observatoire de l'Eau et de l'Erosion aux Antilles. We would like to thank DEAL (especially M. Pellegrinelly-Verdier) for providing hydrological data, and the Parc National de Guadeloupe for field assistance. Thanks are extended to P. Saks and A. White for their help on field. H. Lazard (LGE) and E. Joigneaux (ISTO) are also thanked for their help on C

and N analysis and on the $\delta^{13}\text{C}_{\text{DOC}}$ analysis, respectively. Financial support was provided by INSU-CNRS (PPF OBSERA).

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Figure captions:

Figure 1: Lesser Antilles map with the location of the Guadeloupe, French West Indies.

The inset map shows Basse-Terre Island with simplified pedology and the location of the two studied watersheds (Bras-David and Capesterre).

Figure 2: Carbon isotopic composition of soil organic matter plotted as a function of the $1/C$ ratio (a) and as a function of $\ln C$ (b), with C the TOC content in soil organic matter. Bras-David and Capesterre soil data are represented by circles/solid line, and triangles/dashed line, respectively.

Figure 3: Carbon isotopic composition of DOC in studied rivers for two hydrological stages (low water level and flood) and in soil solutions sampled from lysimeters and obtained by lab extractions. Soil solutions (lysimeters and lab extractions) are

represented by dark grey and light grey symbols for Bras-David and Capesterre, respectively.

Table 1: Watershed characteristics

| Sites | Latitude | Longitude | Area | Elevation | Age of Bedrock ^a | Slopes ^b | | | | Vegetation ^c | | |
|------------|---------------|---------------|------|-----------|-----------------------------|---------------------|--------|--------|--------------|-------------------------|---------------------|------------|
| | | | | | | 0-24% | 25-48% | 49-99% | >99% | Thickets | Altimountain Forest | Rainforest |
| | | | | | | km ² | m | Myrs | % of surface | | | |
| Bras David | N16°10'33.6'' | W61°41'34.8'' | 11.3 | 228-1088 | 1.460 | 38 | 48 | | 0 | | 35 | 65 |
| Capesterre | N16°04'18.0'' | W61°36'34.1'' | 16.6 | 200-1342 | 0.554 | 18 | 32 | 33 | 5 | 33 | 39 | 29 |

^a Samper et al., 2007^b Plaisir et al., 2003^c Rousteau et al., 1994; Rousteau, 1996Table 2: Characteristics of milliQ water and Ca(NO₃)₂ extractions

| Extraction | milliQ water (Bardy, 2008) | Ca(NO ₃) ₂ (Zsolnay, 2003) |
|--|-------------------------------|--|
| Solution/soil (mL g ⁻¹ of dry soil) | 3 | 2 |
| Extraction Time | 12 h | 10 min |
| Centrifugation Time | 20 min | 10 min |

Table 3: Particulate concentrations (TOC, TN), C/N ratios and isotopic compositions of TOC ($\delta^{13}\text{C}_{\text{TOC}}$) for soil solid fraction, and dissolved concentration (DOC), isotopic composition of DOC ($\delta^{13}\text{C}_{\text{DOC}}$) and percentage of aromaticity for liquid fractions obtained by lysimeters and lab extractions (water and $\text{Ca}(\text{NO}_3)_2$) for Bras-David soil.

| Depth cm | Solid fraction | | | | Liquid fraction | | | | | | | |
|-------------|---------------------------|--------------------------|------|---|---------------------------|---|------------------|---------------------------|---|------------------|--|---|
| | TOC g kg^{-1} | TN g kg^{-1} | C/N | $\delta^{13}\text{C}_{\text{TOC}}$ ‰ | Lysimeters | | | Water extractions | | | $\text{Ca}(\text{NO}_3)_2$ extractions | |
| | | | | | DOC mg L^{-1} | $\delta^{13}\text{C}_{\text{DOC}}$ ‰ | Aromaticity % | DOC mg L^{-1} | $\delta^{13}\text{C}_{\text{DOC}}$ ‰ | Aromaticity % | DOC mg L^{-1} | $\delta^{13}\text{C}_{\text{DOC}}$ ‰ |
| Litter | 394.50 | 12.80 | 30.8 | -29.7 | | | | | | | | |
| 0-5 | 91.92 | 5.48 | 16.8 | | | | | | | | 77.92 | |
| 5-10 | 48.66 | 3.91 | 12.5 | -28.0 | | | | | | | | |
| 10-20 | 17.95 | 1.26 | 14.3 | -26.9 | | | | | | | | |
| 20-25 | 17.29 | 1.23 | 14.1 | -27.0 | | | | | | | | |
| 15 | 57.59 | 4.01 | 14.4 | -27.2 | 1.62 | -31.4 | 21.7 | 91.31 | -26.4 | 9.2 | | -28.6 |
| 30 | 32.61 | 2.30 | 14.2 | -27.2 | 0.95 | -33.1 | 32.1 | 55.81 | -26.3 | 7.7 | 57.77 | -28.2 |
| 61 | 8.79 | 0.53 | 16.5 | -26.3 | 1.69 | -31.2 | 17.6 | 8.66 | -27.3 | 9.9 | 12.14 | -25.8 |
| 91 | 7.71 | 0.49 | 15.6 | -26.3 | 0.88 | -33.1 | 18.0 | 8.25 | -28.4 | 11.8 | 10.62 | -26.7 |
| 122 | 3.96 | 0.24 | 16.8 | -26.3 | 0.69 | -32.6 | 24.2 | 6.81 | -27.8 | 12.6 | 7.94 | -26.5 |
| 152 | 2.32 | 0.15 | 15.0 | -26.5 | 0.61 | -33.8 | 31.7 | 6.50 | -27.9 | 12.9 | 7.50 | -26.6 |
| 183 | 1.72 | 0.13 | 13.4 | -25.6 | 0.77 | -33.0 | 24.0 | 3.69 | -27.8 | 19.5 | 4.66 | -26.0 |
| 213 | 1.89 | 0.13 | 14.2 | -25.7 | | | | 5.21 | | 13.7 | 5.90 | -26.6 |
| 244 | 3.71 | 0.24 | 15.6 | -26.8 | | | | 6.76 | | 11.4 | 6.73 | -25.8 |
| 274 | 2.41 | 0.16 | 14.6 | -26.7 | 0.60 | -33.2 | 23.3 | 5.88 | -27.4 | 13.0 | 6.82 | -25.9 |
| 305 | 3.34 | 0.36 | 9.3 | -25.9 | | | | 3.95 | -27.9 | 15.8 | 5.50 | -26.6 |
| 344 | | | | | 0.60 | -33.2 | 24.0 | | | | | |
| 366 | 1.68 | 0.13 | 13.0 | -24.8 | | | | 4.35 | -28.1 | 18.1 | 4.95 | -26.6 |
| 427 | 2.93 | 0.32 | 9.1 | -25.8 | | | | 5.32 | -28.2 | 14.8 | 4.52 | -27.1 |
| 457 | | | | | 0.62 | -33.8 | 23.2 | | | | | |
| 488 | 3.72 | 0.24 | 15.5 | -24.6 | | | | 4.72 | -28.1 | 15.8 | 4.34 | -26.8 |
| 549 | 1.91 | 0.15 | 13.0 | -24.7 | | | | 7.04 | | 12.8 | 5.55 | -27.1 |
| 610 | 1.29 | 0.14 | 9.4 | -26.5 | | | | 6.85 | -28.2 | 13.2 | | -27.0 |
| 671 | 1.72 | 0.18 | 9.7 | -26.4 | | | | 5.44 | | 15.3 | 6.73 | -26.9 |
| 732 | | | | | | | | 4.36 | | 14.5 | 4.22 | -26.9 |
| 792 | 1.30 | 0.13 | 9.9 | -25.7 | | | | 2.92 | | 20.2 | 8.33 | -27.6 |
| 823 | | | | | 0.66 | -32.9 | 28.2 | | | | | |
| 853 | 1.73 | 0.18 | 9.4 | -26.1 | | | | 4.45 | -28.2 | 17.6 | 5.32 | -26.9 |
| 914 | 1.41 | 0.14 | 10.4 | -26.4 | | | | 4.56 | | 15.3 | 7.01 | -27.2 |
| 975 | 0.88 | 0.09 | 9.6 | -24.7 | | | | 3.09 | -28.1 | 17.8 | 5.64 | -27.2 |
| 1036 | 1.14 | 0.10 | 11.8 | -25.1 | | | | 5.67 | | 13.2 | 6.12 | -27.4 |
| 1097 | 1.00 | 0.10 | 9.6 | -27.3 | | | | 5.41 | | 13.0 | 7.32 | -27.6 |
| 1158 | 0.99 | 0.10 | 10.3 | -24.2 | | | | 4.84 | | 14.4 | 6.13 | -26.8 |
| 1219 | 2.51 | 0.34 | 7.3 | -26.2 | | | | 6.92 | | 11.9 | 7.71 | -27.2 |
| 1250 | 2.70 | 0.31 | 8.7 | -25.9 | 0.51 | | 32.6 | 6.65 | -28.2 | 13.5 | 10.69 | -27.5 |

Table 4: Particulate concentrations (TOC, TN), C/N ratios and isotopic compositions of TOC ($\delta^{13}\text{C}_{\text{TOC}}$) for soil solid fraction, and dissolved concentration (DOC), isotopic composition of DOC ($\delta^{13}\text{C}_{\text{DOC}}$) and percentage of aromaticity for liquid fractions obtained by lysimeters and lab extractions (water and $\text{Ca}(\text{NO}_3)_2$) for Capesterre soil.

| Depth cm | Solid fraction | | | | Liquid fraction | | | | | | | |
|-------------|---------------------------|--------------------------|------|---------------------------------------|---------------------------|---------------------------------------|------------------|---------------------------|---------------------------------------|------------------|---|---------------------------------------|
| | TOC g kg ⁻¹ | TN g kg ⁻¹ | C/N | δ ¹³ C _{TOC} ‰ | Lysimeters | | | Water extractions | | | Ca(NO ₃) ₂ extractions | |
| | | | | | DOC mg L ⁻¹ | δ ¹³ C _{DOC} ‰ | Aromaticity % | DOC mg L ⁻¹ | δ ¹³ C _{DOC} ‰ | Aromaticity % | DOC mg L ⁻¹ | δ ¹³ C _{DOC} ‰ |
| Litter | 408.60 | 15.90 | 25.8 | -29.0 | | | | | | | | 73.97 |
| 0-5 | 74.29 | 6.19 | 12.0 | -27.8 | | | | | | | | |
| 5-10 | 53.86 | 5.14 | 10.5 | -27.1 | | | | | | | | |
| 10-15 | 39.05 | 3.65 | 10.7 | -26.5 | | | | | | | | |
| 15-20 | 23.60 | 2.34 | 10.1 | -26.1 | | | | | | | | |
| 20-30 | 20.55 | 1.92 | 10.7 | -26.0 | | | | | | | | |
| 15 | 25.50 | 2.64 | 9.7 | -26.5 | 1.75 | -30.6 | 16.4 | 28.90 | -26.9 | 7.9 | 28.38 | -25.8 |
| 30 | 26.85 | 2.54 | 10.6 | -26.8 | 0.78 | -32.9 | 24.3 | 24.02 | -27.7 | 7.2 | 28.02 | -26.5 |
| 46 | 10.29 | 0.92 | 11.2 | -26.6 | | | | 7.40 | | 9.3 | 5.88 | -26.4 |
| 61 | 7.39 | 0.61 | 12.1 | -25.7 | 0.58 | -33.1 | 32.5 | 6.13 | -28.2 | 14.2 | 4.59 | -26.2 |
| 76 | 5.83 | 0.40 | 14.6 | -25.2 | | | | 4.79 | | 11.6 | 2.95 | -26.5 |
| 91 | 5.63 | 0.44 | 12.9 | -25.7 | 0.76 | -32.8 | 19.3 | 6.35 | -28.3 | 11.8 | 3.24 | -26.4 |

Figure 1

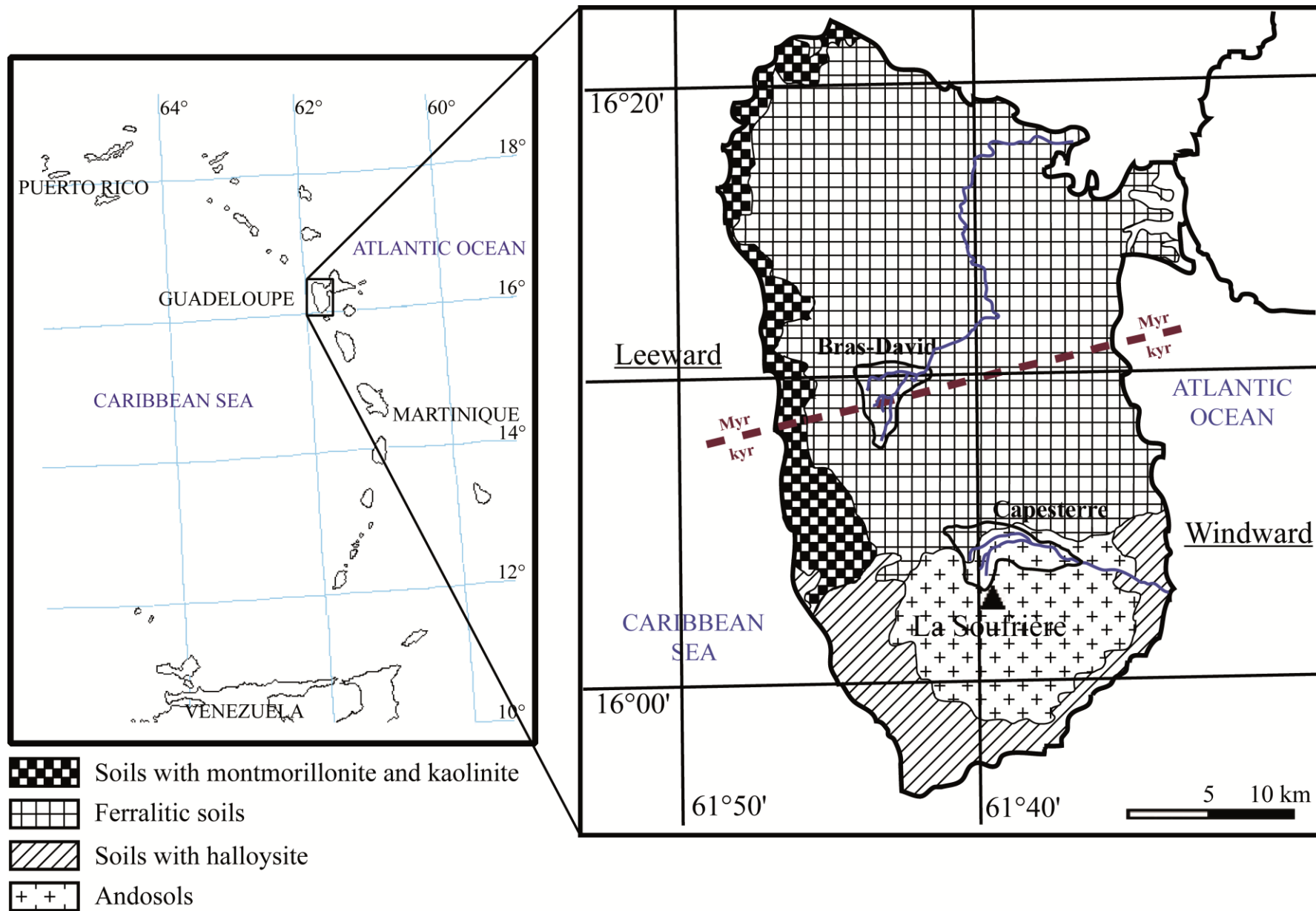


Figure 2a

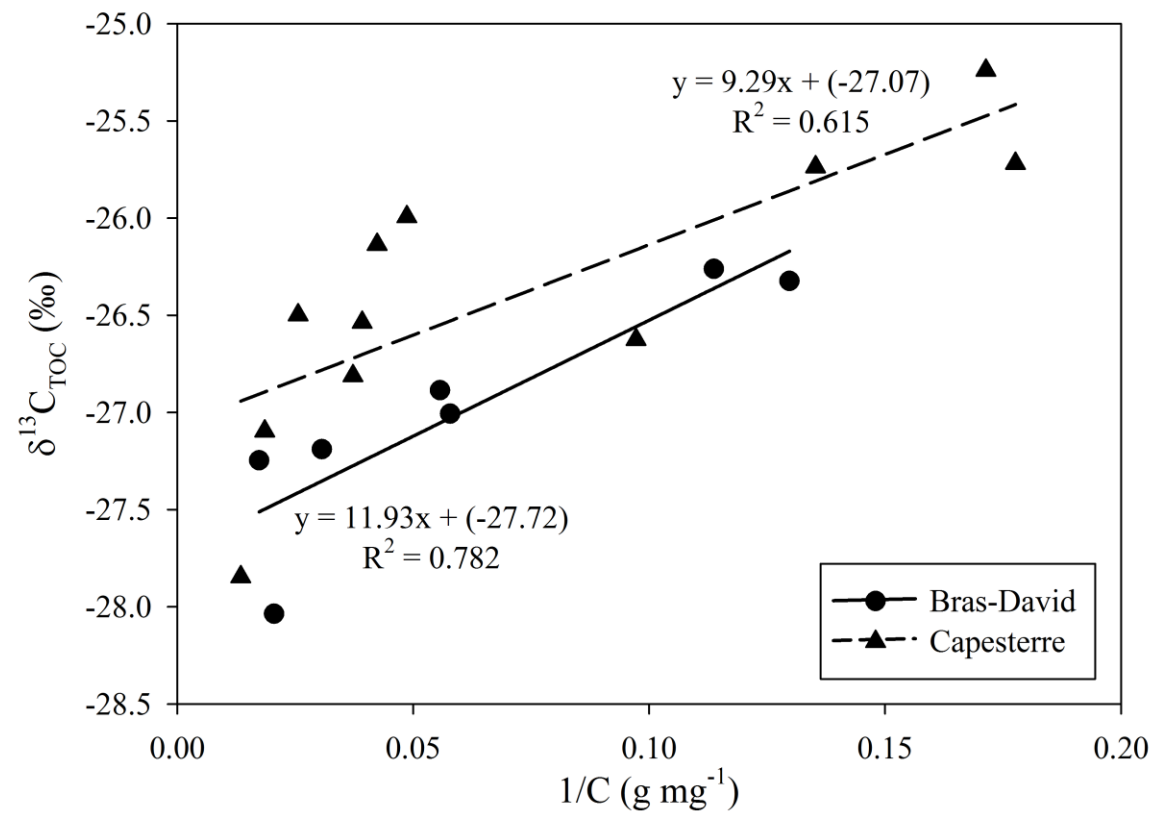


Figure 2b

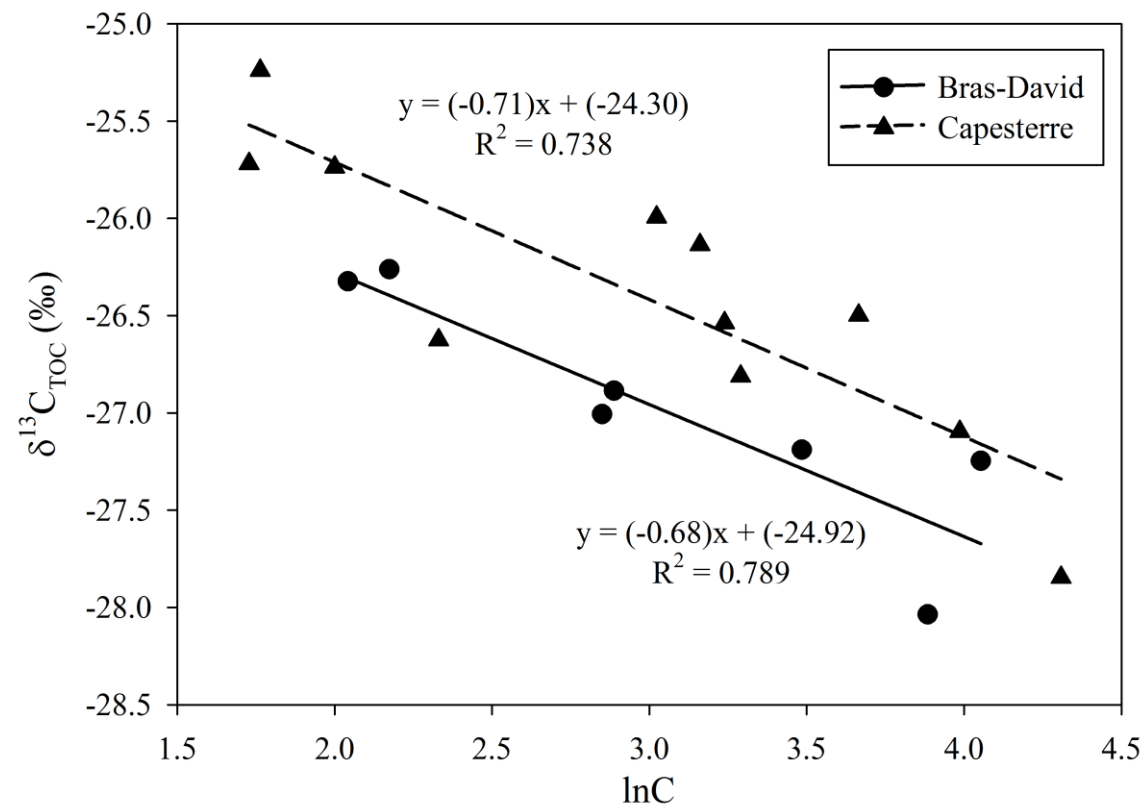


Figure 3

